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Structure-to-Property Relationships in Addition Cured Polymers

IV–Correlations Between Thermo-Oxidative Weight Losses of Norbornenyl Cured Polyimide Resins and Their Composites

William B. Alston
Propulsion Directorate
U.S. Army Aviation Systems Command
Lewis Research Center
Cleveland, Ohio

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By
William B. Alston
Propulsion Directorate
U.S. Army Aviation Systems Command
Lewis Research Center
Cleveland, Ohio 44135

ABSTRACT

The purpose of this study was to identify any relationships between the thermo-oxidative stability (TOS) at 316°C of a wide variety of PMR (polymerization of monomeric reactants) addition cured polyimide resins and their corresponding graphite fiber composites. Weight loss results at 316°C confirmed the expected relationship of increasing aliphatic endcap content with decreasing TOS. More importantly, the resin TOS study also showed an unexpected linear correlation of decreasing weight loss to increasing ratio of benzylic diamine to aliphatic endcap in the range of the stoichiometries studied. Furthermore, only after long-term 316°C aging does the dianhydride used with the benzylic diamines become an additional factor in influencing the amount of PMR resin and composite weight losses. Additionally, the benzylic systems also consistently showed significantly lower resin and composite weight losses at 316°C than the corresponding nonbenzylic/norbornenyl resins and composites, except when the nonbenzylic diamine monomer does not contain a connecting group, e.g., paraphenylenediamine. Instead, this diamine resulted in a 316°C resin and composite weight loss that was only competitive with benzylic type diamines, e.g. 4,4′-diaminotriphenylmethane or 4,4′-diaminodiphenylmethane (methylenedianiline, MDA). The final result of this study showed there is an excellent correlation between the TOS of all the graphite fiber PMR polyimide composites and their corresponding PMR polyimide resins.

INTRODUCTION

As a continuation of a larger investigation (Refs. 1, 2 & 3) directed toward understanding the high temperature oxidative degradation of addition cured polymers, the 316°C weight losses of seventy norbornenyl cured polymerization of monomeric reactant (PMR) polyimide resins and thirty graphite fiber/PMR polyimide composites were determined and compared to each other. The purpose of this portion of the overall study was threefold. The first purpose was to determine which norbornenyl cured PMR composites exhibited the greatest thermo-oxidative stability (TOS) as determined by the amount of long-term 316°C weight loss. The second purpose was to determine if the PMR composites exhibited the same relative ranking of TOS as previously reported (Ref. 1) for the corresponding PMR resins. The third purpose was to determine if the PMR composites exhibited the same structure-to-TOS relationships as previously reported for the PMR resins (Ref. 1). In order to do so, the monomeric composition and the chain length between the norbornenyl crosslinks were systematically varied using PMR technology (Ref. 2) to produce seventy different PMR resins (Ref. 1) and thirty different PMR composites (Ref. 2) for the TOS comparison. The state-of-the-art standard for comparison in this TOS study was PMR-15 resins and PMR-15 composites, both prepared using PMR technology as described in Refs. 1 to 5.

EXPERIMENTAL

PMR Monomer and Polymer Selection

Three dianhydrides, pyromellitic dianhydride (PMDA), 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (HFDA) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) and three mixtures of these dianhydrides were each reacted as their respective diacid-dimethyl esters (PMDE, HFDE, and BTDE) with up to eleven different aromatic diamines and a norbornenyl endcap (Nadic Ester, NE) to prepare the thirty PMR composites (Ref. 2) used for this TOS study. The specific monomers used are shown in Figure 1. The diamines were reacted with the diacid-diesters and a norbornenyl endcap in a ratio of N diacid-diesters/N+1 diamines/2 norbornenyl endcaps. The specific combinations of diacid-diesters and diamines investigated and the N values and formulated molecular weights (FMW) are shown in the legends in Figures 2 to 5 and also shown in Table 1 within Ref. 2.

The compositions investigated were selected on the basis of providing melt processable resins containing a systematic variation in monomer composition and/or stoichiometry (N). All three diacid-diesters and their mixtures were used with 4,4′-diaminodiphenylmethane (methylenedianiline, MDA) and 4,4′-diaminotriphenylmethane (DATPM) as the benzylic type aromatic diamines at N values ranging from 1.367 to 2.65. Other monomer combinations selected were all singular HFDA or BTDA based resins containing a variety of nonbenzylic aromatic diamines at stoichiometries such that a constant FMW of 1500 was maintained. In a few cases where the stoichiometry (N) was varied widely in order to maintain FMW=1500, additional resin compositions were also selected to maintain similar stoichiometries while letting the FMW vary widely. This was done to facilitate weight loss comparisons on a basis of either similar oligomer FMW (similar weight percent aliphatic content) or similar monomer stoichiometry (similar number of imide groups and linkages and similar molar concentration of norbornenyl endcaps while disregarding any similarity in aliphatic norbornenyl endcap weight percent content).

PMR Resin Preparation and Composite Fabrication

The PMR resins used in this comparative study were prepared as described in Ref. 1 using the PMR methodology described in Refs. 1 and 3. Typically, methanol solutions of the three monomers at the prescribed stoichiometry were thermally converted into PMR molding powders. These powders were then thermally cured into resin disks to determine TOS (Ref. 1) and glass transition temperatures (Tg's) (Refs. 2 & 3).

The Celion 6000 graphite fiber/PMR composites used in this comparative TOS study were previously fabricated in Ref. 2. A much more complete description of the typical PMR prepreg preparation and composite processing parameters used are described in Refs. 4 and 5. For this study, typically, the methanol based unidirectional prepreg of unsized Celion 6000 graphite fiber impregnated with the PMR monomer combination at the selected N/FMW value was imidized for one hour at 204°C as a 12 ply 3 by 8 inch prepreg stack. The ply stack was then cured by the standard PMR compression molding techniques; i.e., two hours at 316°C at up to 2000 psi. All the PMR composites were postcured by the standard PMR-15 postcure process, a free-standing postcure in 316°C air for sixteen hours, before undergoing TOS evaluation. Ultrasonic C-scans and photomicrographs were obtained to verify the resultant PMR composites were of acceptable quality for TOS comparison with their corresponding PMR resins.

The thirty 3 x 8 inch PMR composites were then cut into nine 1 x 2-1/2 inch test coupons. Two of these coupons, usually from the composite ends, were used to determine the initial room temperature and 288°C or 316°C interlaminar shear strength and flexural strength of the composites (Ref. 2) for use as supporting evidence of the quality of the composites. Additionally, these initial composite mechanical properties (Ref. 2) were correlated with Tg and mechanical test temperature (Ref. 6) as additional supporting evidence of the acceptable composite quality before initiating the composite TOS study.

Resin and Composite Isothermal Aging

The long-term aging of PMR neat resins was done for up to 2000 hours of 316°C ± 1°C air exposure on four similar sized PMR resin pieces cut from each resin disk. All the resins were aged simultaneously and along with their respective composites in a circulating air oven having an air change rate of 100 cm^3/minute. During this time the dimensional and weight changes were monitored to determine weight loss per unit surface area as a function of aging time. The methodology (Ref. 4) to obtain the weight losses, standard deviations and the weight loss/surface area were previously reported (Ref. 1).

The long-term aging of PMR composites was done for up to 2800 hours of 316°C ± 1°C air exposure using the remaining seven of the initial nine test coupons from each PMR laminate. All the composites were aged simultaneously and along with their respective PMR resins in a circulating air oven having an air change rate of 100 cm^3/minute. The only exceptions were the four BTDA composites (Ref. 5), shown in Figure 2, that were aged together for up to 2100 hours, but at a different time than the balance of this study. Composite weight losses were determined every 100 hours for the first 400 hours and every 200 hours thereafter (150 hours for the BTDA exceptions). After each weighing the position of the test coupons in the aging oven was systematically varied to average out any potential errors due to temperature variations within the oven. Every 400 hours (300 hours for the BTDA exceptions) one test coupon per laminate was removed for future mechanical testing. The coupon with the highest or next highest weight loss was always removed to minimize the data scatter. Thus, the number of test coupons for each composite aged decreased sequentially from seven to one in 300 or 400 hour intervals until the final aging data point was a single value without a standard deviation.

Composite Weight Loss Data Treatment

The composite weight loss data was reported on a percent weight loss basis because: (1) each test coupon has approximately the same surface area and weight and (2) the data would be more readily comparable to prior literature PMR composite TOS data. All the composite weight losses shown in Figures 2 to 5 only show the standard deviation when one sigma exceeds the size of the symbol used in the figures. Also, to do accurate weight loss comparisons between any composites the fiber/resin contents should be similar. Thus, the weight of each postcured composite in Figures 2 to 5 is identified beside the N/FMW values in each figure legend; 34.18 g. of which is the calculated fiber weight with the balance being resin so that weight loss comparisons can be done at similar resin contents. To further aid in weight loss comparisons, the curves in Figures 2 to 5 are in the exact same order as the legends, except for the PMDA PMR-15 and PMDA PMR-13 curves (shown as solid triangle and solid diamond symbols) which are superimposed on top of the PMR-15 to PMR-13.5 curves which are in the order given in the legend in Figure 3.

RESULTS AND DISCUSSIONS

Weight Losses of BTDA-PMR Composites and Resins

Figure 2 shows the 316°C percent weight loss of twelve BTDA-PMR composites using eight different diamines, all at similar FMW (1500) and fiber/resin contents (48 to 53 g. composites) except for two composites kept at the same stoichiometry (N = 2.0) while letting FMW increase from 1500 to 1756 and 1950.

These TOS results show that as the aliphatic norbornenyl content increases (the lower two lines), the 316°C composite weight loss slowly increases. Also observed was the use of MDA or DATPM for the benzylic type PMR composites (the lower five lines) provides about the same range of composite weight losses. Furthermore, the nonbenzylic PMR composites all exhibit greater weight losses (upper seven lines) than the benzylic PMR composite weight losses (lower five lines), which agrees with prior PMR composite results using 3FDAM and ODA versus MDA (Ref. 5). These three PMR composite results completely agree with the previously reported PMR resin results (Ref. 1).

Weight Losses of PMDA/BTDA-PMR Composites and Resins

Figure 3 shows the 316°C percent weight losses for two PMDA composites (PMDA PMR-13, and PMDA PMR-15), one BTDA composite (PMR-15) and three mixed PMDA/BTDA composites (such as 50/50 P/B = 50% PMDA / 50% BTDA = PMR-14), all with MDA as the aromatic diamine and all at similar fiber/resin contents (51 to 54 g. composites). For Figure 3, N was kept constant so FMW decreased from 1500 to 1300 (except for the N=2.65/FMW=1500 PMDA PMR-15 composite).

These TOS results show as the aliphatic norbornenyl content slowly increases from PMR-15 (100% BTDA) to PMR-13.5 (25% BTDA while N remains constant at 2.087), the 316°C composite weight loss also slowly increases (open symbols). This finding is in total agreement with the PMR resin weight losses in Ref. 1. However, as 100% PMDA is attained in PMDA PMR-13 and PMDA PMR-15 (solid symbols) the TOS trend reversed such that the weight loss of PMDA PMR-13 approximates BTDA PMR-15 while the PMDA PMR-15 weight loss increased to above PMDA PMR-13 weight loss. This trend reversal may be because the amount of aliphatic remaining after processing could easily be less as both 100% PMDA based composites required a considerably higher processing temperature than PMR-13.5 to PMR-15 and also the PMDA PMR-15 composite was clearly of a poorer quality due to processing problems.

However, the TOS trend for PMDA-PMR resins was completely consistent with changes in N value and aliphatic norbornenyl content previously reported for all PMR resins (Ref. 1). Thus, TOS of PMR resins decreased when PMDA PMR-15 was changed to BTDA PMR-15 (N value lowers, so aliphatic content is constant) which was then changed to PMDA PMR-13 (N value constant so as FMW lowers, aliphatic content increases). Thus, for PMR resins the TOS of PMDA PMR-15 > BTDA PMR-15 > PMDA PMR-13; while for composites BTDA PMR-15 > PMDA PMR-13 > PMDA PMR-15. The lower TOS of PMDA-PMR composites is probably due to difficulty in processing good quality 100% PMDA composites, particularly as N increases to 2.65 in PMDA PMR-15.

More importantly because the benzylic/norbornenyl ratio is constant (except N = 2.65) all the 316°C composite weight losses are grouped closely together in Figure 3. They also virtually coincide with the weight losses for benzylic BTDA composites (lowest line in Figure 3 and all five lower lines in Figure 2). Thus, the TOS of benzylic PMDA composites are virtually equal to those of benzylic type BTDA composites. This result is in reasonable agree-

ment with the PMR resin TOS data in which benzylic PMDA-PMR resins had slightly better TOS than benzylic type BTDA-PMR resins (Ref. 1).

Weight Losses of HFDA-PMR Composites and Resins

Figure 4 shows the 316°C percent weight loss of ten HFDA-PMR composites using seven different diamines, all at similar FMW (1500) and fiber/resin contents (48 to 53 g. composites) except for the benzylic type composites covering FMW 1320 to 2000 (N = 1.367 to 2.49) and the FMW = 1263 (N = 1.67) PPDA composite and the 42.3 g. 4,4′-DABP composite. To simplify Figure 4, seven weight loss curves were not shown as follows: (1) a FMW = 1500 DAFO and a FMW = 1500 stilbene curve both much higher than any other curves shown, (2) a 3,3′-DABP curve that coincided with the 4,4′-DABP curve shown, (3) a FMW = 1800 EDA curve slightly above the FMW = 1500 EDA curve shown, (4) a FMW = 1500 DAF curve slightly above the N = 1.66 ODA curve shown, (5) a N = 1.367 DATPM curve that coincided with the N = 1.367 MDA curve and (6) a N=2.087 MDA curve that coincided with the N=2.087 DATPM curve.

The TOS results show that as the aliphatic norbornenyl content increases and N decreases in the lower four lines the 316°C composite weight loss slowly increases. Also observed was that the use of MDA or DATPM at the same N value for the benzylic type PMR composites provides virtually identical composite weight losses, as well as the lowest composite weight losses in the entire TOS study. These three PMR composite results completely agree with the previously reported results for benzylic type HFDA-PMR resins (Ref. 1).

The next most TOS HFDA-PMR composites were based on paraphenylenediamine (PPDA). Again as aliphatic norbornenyl content increases, the TOS slightly decreases; which is in total agreement with the PMR resin data (Ref. 1). It is important to note the stable HFDA/PPDA monomer combination closely competes in TOS with the benzylic HFDA-PMR resin for up to 2000 hours at 316°C (Ref. 1); indeed even competes for the first 500 hours with the benzylic BTDA-PMR resin (PMR-15 in Refs. 1 & 7). Thus, at extended 316°C aging the TOS of PMR resins and composites agree as both exhibit TOS of benzylic type HFDA = HFDA/PPDA PMR > benzylic type BTDA-PMR = benzylic type PMDA-PMR.

The next most TOS HFDA-PMR composites were based, surprisingly, on ethylenedianiline (EDA) because the ethylene linkage thermally easily forms two benzyl radicals. This would break the polymer chain to presumably result in weight loss. However, the recombination and/or crosslinking must be more extensive than expected to give the surprisingly low composite weight loss. This PMR composite TOS result also agrees with the PMR resin results (Ref. 1).

The least TOS HFDA-PMR composites are those with presumably the more oxidatively stable diamines (upper three lines) which would normally be predicted to give the best TOS. This unexpected result agrees with the nonbenzylic BTDA-PMR composites also resulting in the greatest composite weight losses in Figure 2 (and also as reported in prior work in Ref. 5). This PMR composite TOS result is also in total agreement with the HFDA-PMR resin result (Ref. 1).

A comparison of the lower group of curves in Figures 2 to 4 is shown as Figure 5. This comparison provides the observation that at comparable benzylic/aliphatic ratios the TOS of HFDA PMR > PMDA PMR = BTDA PMR > all nonbenzylic PMR containing a diamine with a connecting linkage. This is in good agreement with the benzylic PMR resin conclusions (Ref. 1) of TOS of HFDA PMR > PMDA PMR > BTDA PMR > all nonbenzylic PMR containing a diamine with a connecting linkage. In addition the HFDA/PPDA PMR linkage closely competes to the benzylic HFDA-PMR.

CONCLUSIONS

From these results the following may be concluded about the thermo-oxidative weight losses of norbornenyl cured polymerization of monomeric reactants (PMR) graphite fiber composites and their corresponding PMR resins:

1. The 316°C composite weight loss always decreases with decreasing aliphatic content (increasing formulated molecular weight, FMW). More importantly 316°C composite weight loss decreases in direct correlation to increasing stoichiometry (increasing N) over a wide range of compositions for benzylic type PMR composites, e.g. containing 4,4′-diaminodiphenylmethane (methylenedianiline, MDA) or 4,4′-diaminotriphenylmethane (DATPM). This PMR composite conclusion was previously extensively proven for the corresponding PMR resins (Ref. 1).

2. The 316°C composite weight losses of benzylic/norbornenyl cured PMR composites is primarily a function of the amount of the benzylic type diamine, not the dianhydride. Thus, at the same N value the composite weight losses in MDA and DATPM-PMR composites are virtually identical. However, as the 316°C exposure time increases, a secondary factor of the thermo-oxidative stability of the dianhydride is observed superimposed on top of the benzylic/norbornenyl thermo-oxidative stability factor. Thus the long-term 316°C thermo-oxidative stability of benzylic type PMR composites based on various dianhydrides is HexaFluoropropane Diphthalic Anhydride > Pyromellitic Dianhydride = Benzophenone Tetracarboxylic Dianhydride (HFDA > PMDA = BTDA). This PMR composite conclusion was previously reported for the corresponding benzylic type PMR resins (Ref. 1) as HFDA > PMDA > BTDA.

3. The 316°C composite weight loss for nonbenzylic/norbornenyl cured PMR composites only competes with the benzylic/norbornenyl PMR composites when the composites are based on HFDA using diamines without a connecting group (e.g. paraphenylenediamine, PPDA). All the other nonbenzylic/norbornenyl cured PMR composites exhibit greater weight losses than either the benzylic type/norbornenyl cured PMR composites or nonbenzylic/norbornenyl cured PMR composites based on very stable monomer combinations as in HFDA/PPDA. Thus, the use of more oxidatively stable diamines that contain nonbenzylic connecting linkages in norbornenyl PMR composites leads to greater 316°C weight loss, which agrees with the previous PMR composite results (Ref. 5). These PMR composite conclusions were also previously reported for the corresponding PMR resins (Ref. 1).

4. A comparison of the benzylic versus nonbenzylic PMR composite 316°C weight losses shows benzylic weight losses are invariably much less than the nonbenzylic weight losses, except for HFDA/PPDA PMR composites. The weight loss of HFDA/PPDA PMR composites is competitive, but slightly higher, than the weight loss of HFDA/benzylic type composites. These same structure-to-thermo-oxidative stability relationships were also previously reported for the corresponding PMR resins (Ref. 1).

5. As a summary of the above four conclusions, there exists an excellent correlation between the thermo-oxidative stability results of all the graphite fiber PMR polyimide composites and their corresponding PMR polyimide resins.

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BIOGRAPHY

Dr. William B. Alston received his B.S. in Chemistry from the University of Wisconsin, M.S. and Ph.D. in Chemistry from the University of Iowa. He is a civilian Materials Research Engineer with the Propulsion Directorate of the U.S. Army Aviation Systems Command, assigned to the Polymers Branch of the NASA-Lewis Research Center since 1971. His current research is in the high temperature polymer composite areas of monomer and polymer synthesis, cross-linking methods and matrix resin characterization. His publications include 28 papers related to organic chemistry, polymer chemistry, and composite fabrication/characterization, primarily in the areas of PMR polymers, PMR composites and high molecular weight 3F condensation polyimides. He is a member of the American Chemical Society (ACS) and the Society for the Advancement of Material and Process Engineering (SAMPE) and is the recipient of the Best Paper Award at a 1980 SAMPE Conference. He is also a coinventor on Second Generation PMR Polyimides, which received an IR·100 Award in 1977, and five U.S. patents for 3F Condensation Monomers and Polymers.

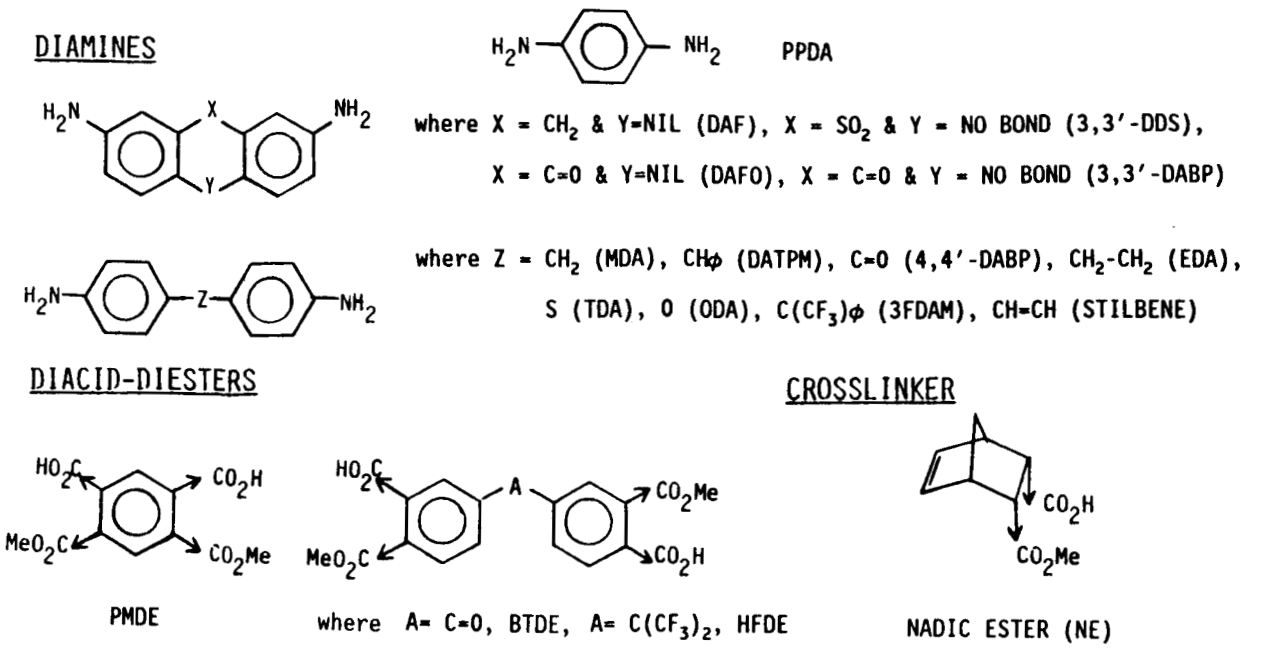

Figure 1. Monomers Used in PMR Composites.

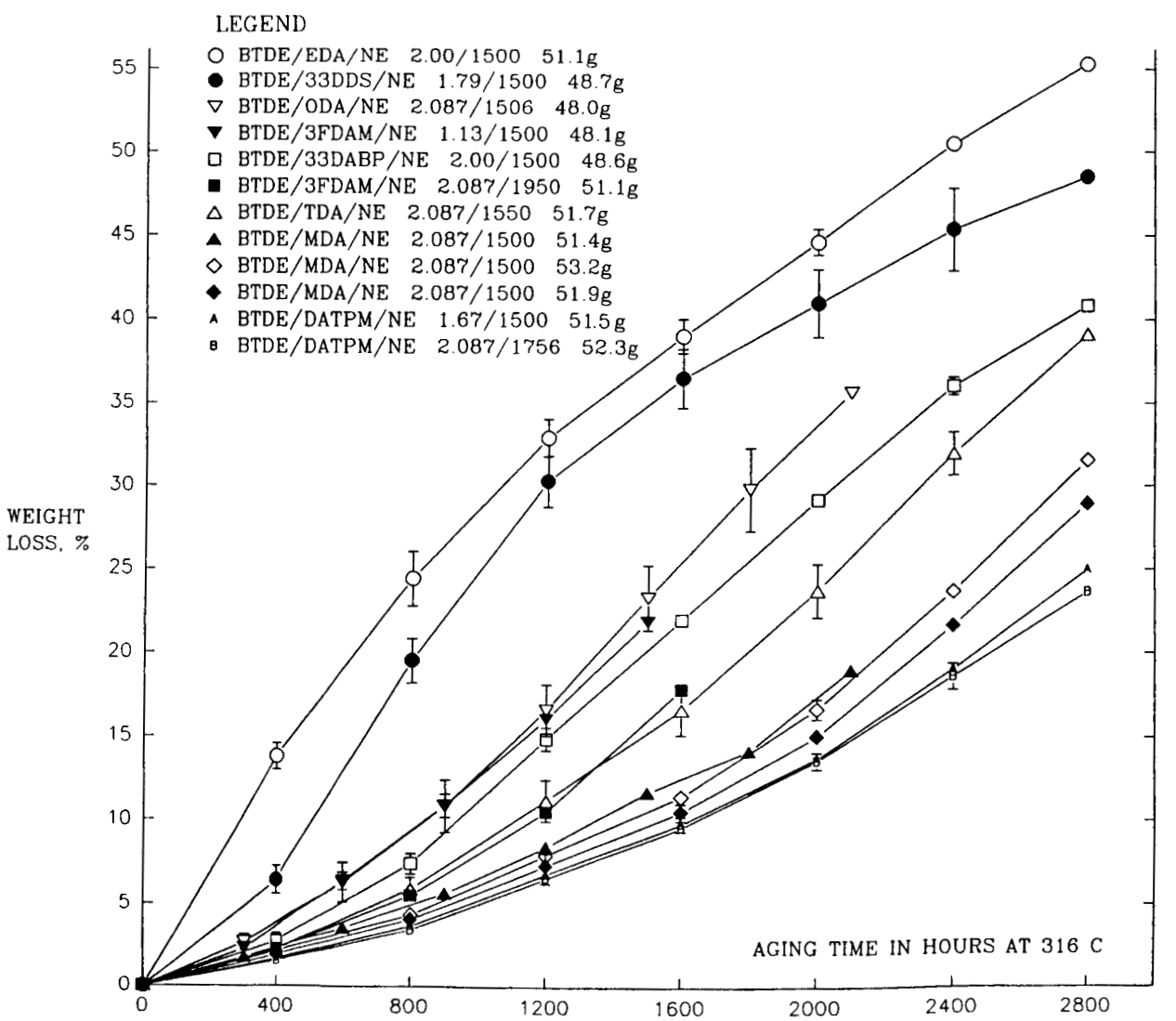

Figure 2. 316°C Percent Weight Losses of BTDE-PMR Composites.

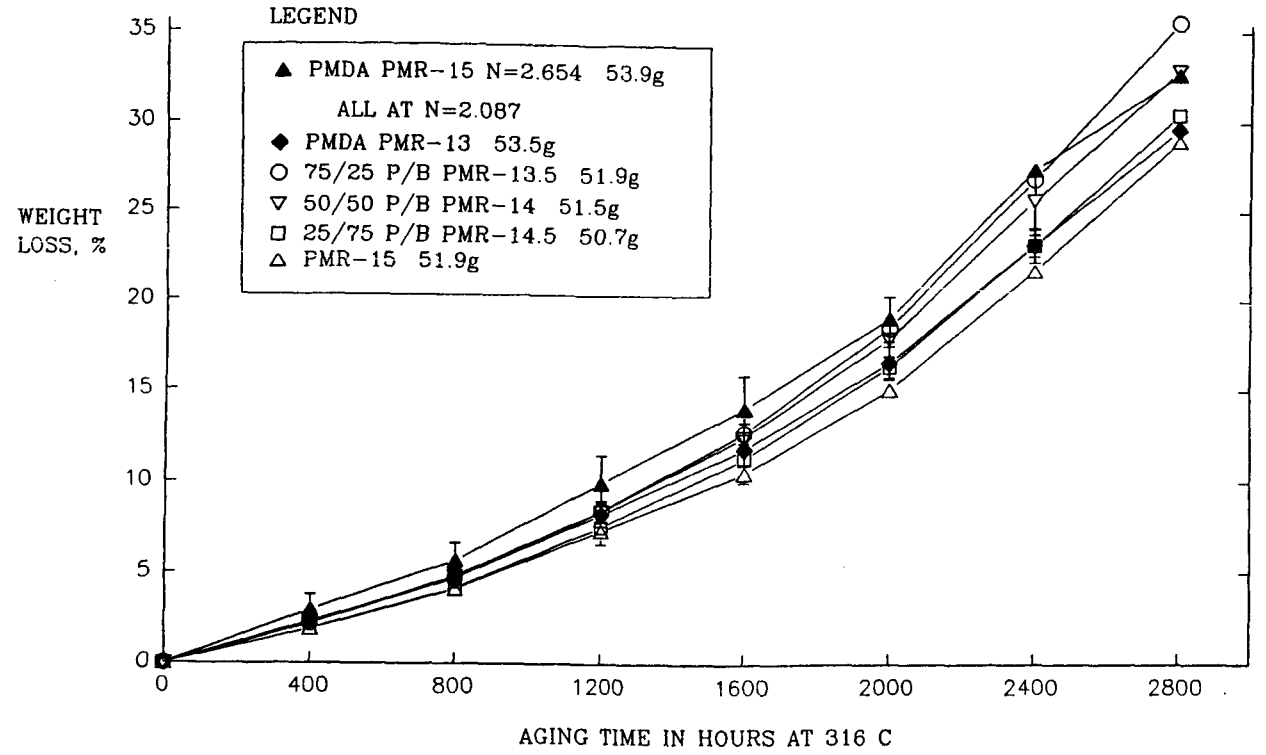

Figure 3. 316°C Percent Weight Losses of PMDE/BTDE-PMR Composites.

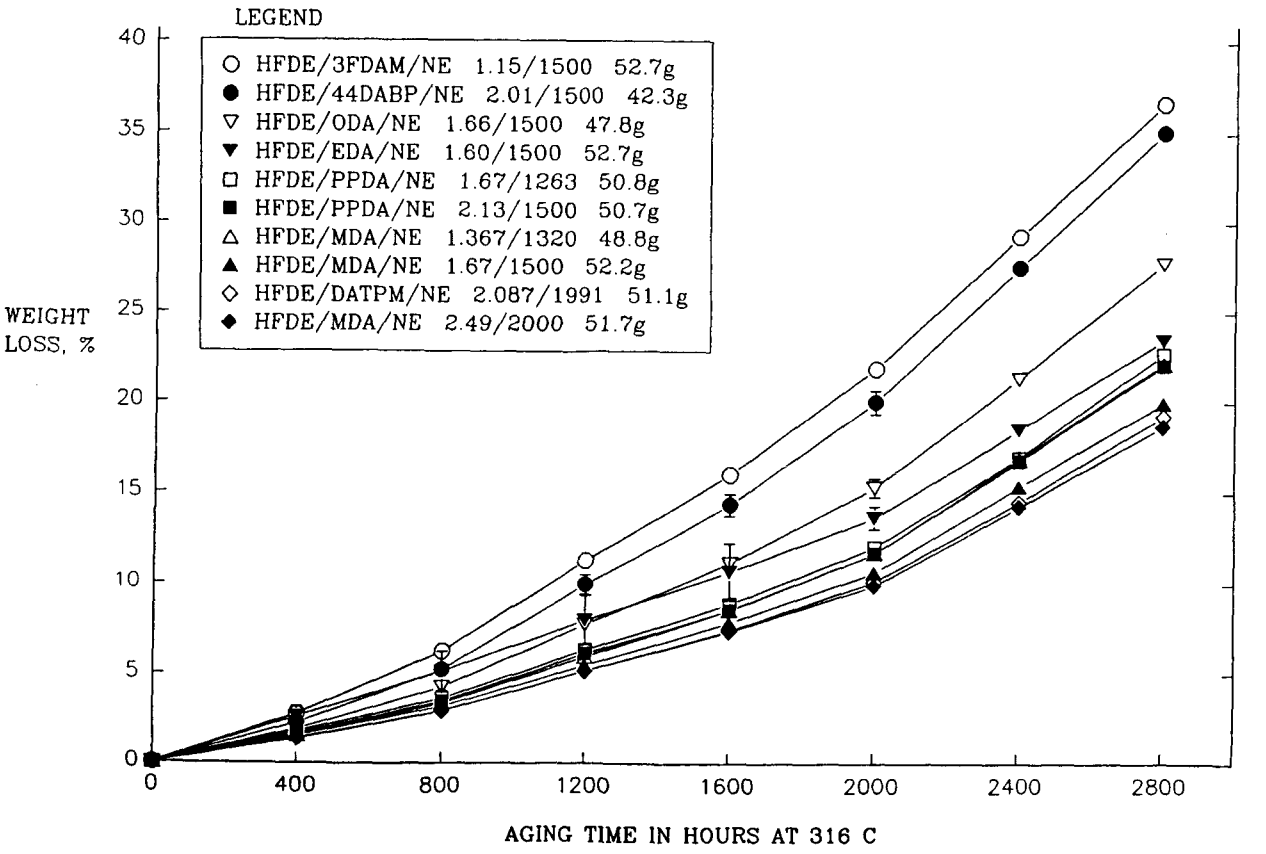

Figure 4. 316°C Percent Weight Losses of HFDE-PMR Composites.

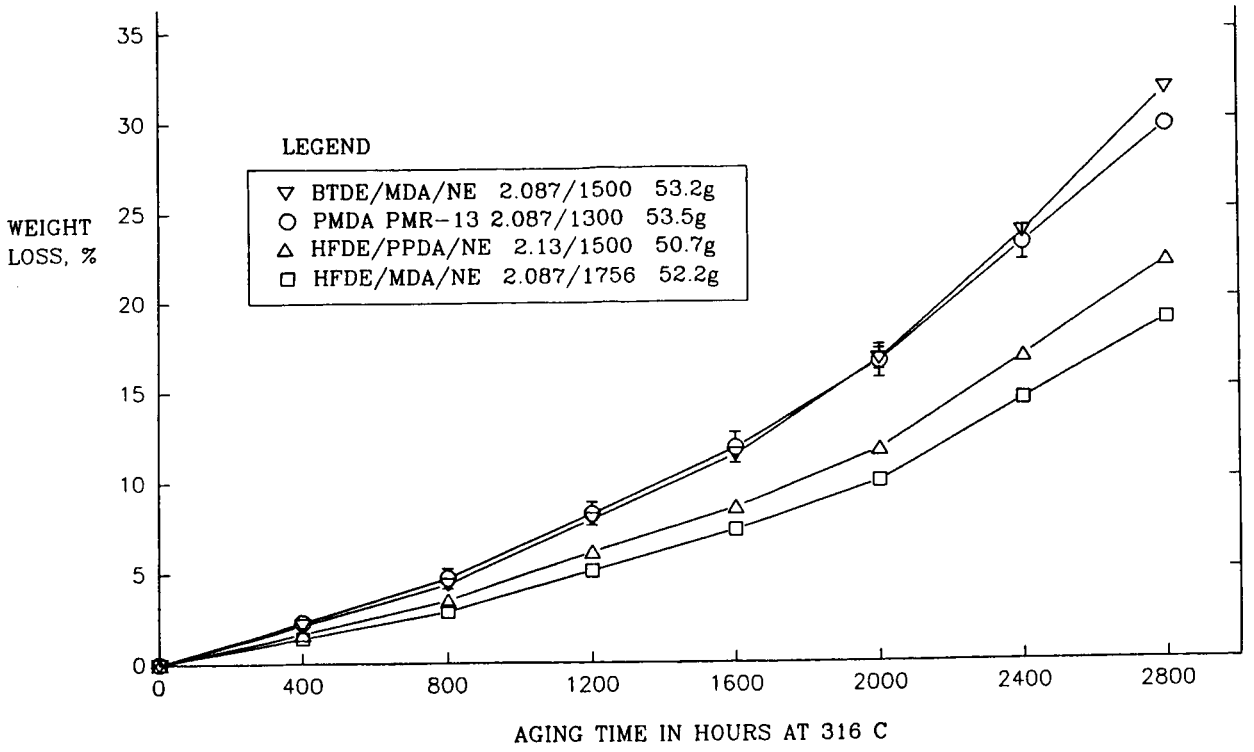

Figure 5. Lowest 316°C Percent Weight Losses of PMR Composites.

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13. ABSTRACT *(Maximum 200 words)*

The purpose of this study was to identify any relationships between the thermo-oxidative stability (TOS) at 316°C of a wide variety of PMR (polymerization of monomeric reactants) addition cured polyimide resins and their corresponding graphite fiber composites. Weight loss results at 316°C confirmed the expected relationship of increasing aliphatic endcap content with decreasing TOS. More importantly, the resin TOS study also showed an unexpected linear correlation of decreasing weight loss to increasing ratio of benzylic diamine to aliphatic endcap in the range of the stoichiometries studied. Furthermore, only after long-term 316°C aging does the dianhydride used with the benzylic diamines become an additional factor in influencing the amount of PMR resin and composite weight losses. Additionally, the benzylic systems also consistently showed significantly lower resin and composite weight losses at 316°C than the corresponding nonbenzylic/norbornenyl resins and composites, except when the nonbenzylic diamine monomer does not contain a connecting group, e.g., paraphenylenediamine. Instead, this diamine resulted in a 316°C resin and composite weight loss that was only competitive with benzylic type diamines, e.g. 4,4′-diaminotriphenylmethane or 4,4′-diaminodiphenylmethane (methylenedianiline, MDA). The final result of this study showed there is an excellent correlation between the TOS of all the graphite fiber PMR polyimide composites and their corresponding PMR polyimide resins.

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